

## Patent Abstracts of Japan

PUBLICATION NUMBER : 2000024691  
PUBLICATION DATE : 25-01-00

APPLICATION DATE : 09-07-98  
APPLICATION NUMBER : 10194167

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INT.CL. : C02F 5/10 C02F 5/00 C08F 8/00 C08F 8/14 C08F 20/04 C08F 22/00 C08F290/06  
C23F 14/02

TITLE : WATER-SOLUBLE COPOLYMER (SALT) AND SCALE INHIBITOR

ABSTRACT : PROBLEM TO BE SOLVED: To obtain a superior scale inhibiting effect to silica scale by using a water-soluble copolymer contg. constituent units having a carboxylic acid group and constituent units having a polyalkylene oxide group as the repeating constituent units and setting the wt. average mol.wt. within a specified range.

SOLUTION: This water-soluble copolymer contains constituent units having a carboxylic acid group such as maleic anhydride, acrylic acid, methacrylic acid,  $\alpha$ -haloacrylic acid, itaconic acid, vinylacetic acid, allylacetic acid, fumaric acid or phosphinocarboxylic acid and constituent units having a polyalkylene oxide group such as (alkoxy)polyethylene glycol mono(meth)acrylate, (alkoxy) polypropylene glycol mono(meth)acrylate or (alkoxy)polyethylene glycol polypropylene glycol mono(meth)acrylate groups as the repeating constituent units and sets the wt. average mol.wt. to >50,000 to 3,000,000.

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<p>2000-175539/16 A97 D15 M14 (A14 A25) JAPS 1998.07.09  NIPPON GOSSEI GOMU KK *JP 2000024691-A  1998.07.09 1998-194167(+1998JP-194167 2000.07.25) C02F 5/10,  5/00, C08F 8/00, 8/14, 20/04, 22/00, 29/06, C23F 14/02  Water-soluble copolymer or salt used in scale inhibitor -  comprising carboxylic acid gp. and polyalkylene oxide gp.  structural units  C2000-054782</p>	<p>A(4-F1A, 10-E1, 12-W11D, 14-A3A) M(14-F)</p>
<p>NOVELTY - A water-soluble copolymer or salt contains: (a) a  constituent unit having a carboxylic acid group; and (b) a constituent  unit having a polyalkylene oxide group. The water-soluble copolymer  or salt has a weight-average molecular weight of more than 50,000  and 3,000,000 or less.</p> <p><u>USE</u>  The water-soluble copolymer or salt is used in scale inhibitors and  controls the adhesion of water-based scales, particularly, silica-based  scales.</p> <p><u>ADVANTAGE</u>  Specifying the functional groups and macromolecular weight  evolves synergism and exerts superior scale prevention. The water-</p>	<p>soluble copolymer (salt) has high scale prevention, particularly,  relative to the silica-based scales. The scale prevention is retained for  a long period of time.</p> <p><u>POLYMERS</u>  The scale inhibitor uses the water-soluble copolymer (salt) as its  effective component.  Preferred water-soluble copolymer (salt) is obtained by  polymerizing a monomer component using the following as its  principal constituents: (a) a monomer having a double bond  containing the carboxylic acid group and capable of polymerization;  and (b) a monomer having a double bond containing the polyalkylene  oxide group and capable of polymerization.  The weight ratio of (a) to (b), (a)/(b), is 40-98/20-60 where, (a) +  (b) = 100 percent by weight.  (8pp215DwgNo.0/0)</p> <p>JP 2000024691-A</p>

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(19) JAPANESE PATENT OFFICE (JP)

(11) Publication Number

(12) THE LAID-OPEN PATENT GAZETTE (A)

2000-24691

(P2000-24691A)

(43) Publication date: 25 January 2000

(51) Int. Cl.	Identification Code	FI	Theme Code (Ref).
C 02 F 5/10	620	C 02 F 5/10	620C 4J005
5/00	620	5/00	620C 4J100
C 08 F 8/00		C 08 F 8/00	4K062
8/14		8/14	
20/04		20/04	

Request for examination: Not received

Number of claims: 11: OL (Total 8 sheets) Continued on final page

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(54) [Title of Invention] WATER SOLUBLE COPOLYMER (SALT)  
AND SCALE INHIBITOR

(57) [Abstract]

[Problem] To provide a water soluble copolymer (salt) with better scale-inhibiting effects than conventional materials and in particular, outstanding scale-inhibiting effects even against silica-based scale.

[Solution] A water soluble copolymer (salt) containing (a) a structural unit having a carboxylate group and (b) a structural unit having a polyalkylene oxide group as repeating structural units and also with weight average molecular weight exceeding 50,000 but not more than 3,000,000.

[Claims]

[Claim 1] A water soluble copolymer (salt) containing (a) a structural unit having a carboxylate group and (b) a structural unit having a polyalkylene oxide group as repeating structural units and also with weight average molecular weight exceeding 50,000 but not more than 3,000,000.

[Claim 2] The water soluble copolymer (salt) of Claim 1 obtained by copolymerizing monomer components comprising principally (a) a monomer containing a carboxylate group with a polymerizable double bond and (b) a monomer containing a polyalkylene oxide group with a polymerizable double bond.

[Claim 3] The water soluble copolymer (salt) of Claim 1 or 2 wherein the ratio by weight of (a)/(b) is 40~98/2~60 [such that (a)+(b) = 100 wt %].

[Claim 4] The water soluble copolymer (salt) of Claim 1 or 2 wherein the ratio by weight of (a)/(b) is 50~98/2~50 [such that (a)+(b) = 100 wt %] and moreover the value of A expressed by the following formula exceeds 25 but is not more than 3,000,000.

$$A = [(Mw/10,000)^4 \times (\text{wt \% of polyalkylene oxide group-containing structural units within total repeating structural units})] / 1000$$

(wherein Mw denotes weight average molecular weight)

[Claim 5] The water soluble copolymer (salt) of Claim 1 or 2 wherein the degree of polymerization of the polyalkylene oxide constituting (b) is 2~50.

[Claim 6] A scale inhibitor whose active ingredient is a water soluble copolymer (salt) described in any of Claims 1~5.

[Claim 7] The scale inhibitor of Claim 6 wherein the scale is silica-based scale.

[Claim 8] A method of producing a water soluble copolymer (salt) described in any of Claims 1~5 characterized in that:

- ① monomer components comprising principally (a) a monomer containing a carboxylate group with a polymerizable double bond and (b)-1 a monomer containing a polyalkylene oxide group with a polymerizable double bond are polymerized; or
- ② during or after the polymerization of a monomer component comprising principally (a), a polyalkylene oxide (b)-2 is introduced by esterification; or
- ③ during or after the polymerization of monomer components comprising principally component (a) above and an active hydrogen-containing monomer, an alkylene oxide (b)-3 is reacted to introduce polyalkylene oxide groups, so as to give weight average molecular weight exceeding 50,000 but not more than 3,000,000.

[Claim 9] The method of producing a water soluble copolymer (salt) of Claim 8 wherein the ratio by weight of component (a) / component (b) [(b)-1, (b)-2 or (b)-3] is 40~98/2~60 [such that (a)+(b) = 100 wt %].

[Claim 10] The method of producing a water soluble copolymer (salt) of Claim 8 wherein the ratio by weight of component (a) / component (b) [(b)-1, (b)-2 or (b)-3] is 50~98/2~50 [such that (a)+(b) = 100 wt %] and moreover the value of A expressed by the following formula exceeds 25 but is not more than 3,000,000.

$$A = \{ (Mw/10,000)^4 \times [(wt \% \text{ of } (b) \text{ within } (a) \sim (b))] \} / 1000$$

(wherein Mw denotes weight average molecular weight)

[Claim 11] The method of producing a water soluble copolymer (salt) of Claim 8 wherein the degree of polymerization of the polyalkylene oxide is 2~50.

[Detailed description of the invention]

[0001]

[Technical field to which the invention belongs] The present invention relates to water soluble copolymers (salts) capable of controlling the problem of the build-up of scale, and especially silica-based scale, in water systems and to scale inhibitors taking these copolymers as active ingredients.

[0002]

[Prior art] Scale made of calcium salts, magnesium salts, silica and the like forms on the walls of vessels which come into contact with water, such as cooling water systems and boiler water systems and especially electrically heated surfaces. In particular, in the high concentration operation of open circuit types of cooling water system in which the wastage (blowing) of cooling water outside the system is reduced from the standpoint of resource and energy saving, the dissolved salts are at high concentrations and the low solubility calcium salts, magnesium salts and silica etc. form scale. Silica is of particularly low solubility amongst these, forming scale at around 100-150 mg/L. Existing proposals for scale inhibitors to prevent or remove the build-up of such silica-based scale include poly(meth)acrylates (e.g. Japanese Examined Patent 49-30914 (1974)). Whilst scale inhibitors using existing polymer compounds as their active ingredients can be outstandingly effective in limited ranges of applications, they are not always satisfactory. In particular, in the high concentration operation of open-circuit cooling water systems, the existing technology is not satisfactory for preventing the build-up of silica-based scale and scale inhibitors providing more effective scale control are being demanded.

[0003]



[Problem to be solved by the invention] The present invention seeks to solve the existing problems and introduce a water soluble copolymer (salt) with superior scale-inhibiting performance to conventional materials and which, in particular, is outstandingly effective even against silica-based scale.

[0004]

[Solution] Following painstaking research on ways of solving the problems inherent with the above types of scale inhibitor, the present inventors discovered that extremely superior scale-inhibiting effects could be achieved by using high molecular weight water soluble copolymers (salts) which simultaneously satisfy conditions (1) and (2) below, even without the concomitant use of certain specific low molecular weight compounds. The present invention is based on this information.

(1) a water soluble copolymer (salt) having a carboxylate group and polyalkylene oxide group as essential components

(2) a water soluble copolymer (salt) with weight average molecular weight exceeding 50,000

[0005] In essence, the present invention provides a water soluble copolymer (salt) containing (a) a structural unit having a carboxylate group and (b) a structural unit having a polyalkylene oxide group as repeating structural units and also with weight average molecular weight exceeding 50,000 but not more than 3,000,000. Herein, it is desirable for the above water soluble copolymer (salt) to be obtained by copolymerizing monomer components comprising principally (a) a monomer containing a carboxylate group with a polymerizable double bond [hereinafter termed 'component (a)' or 'carboxylate group-containing monomer (a)'] and

(b) a monomer containing a polyalkylene oxide group with a polymerizable double bond [hereinafter termed 'component (b)' or 'polyalkylene oxide group-containing monomer (b)']. The present invention also introduces scale inhibitors which take the above water soluble copolymers (salts) as their active ingredient. As the above scale inhibitors have high levels of inhibitory activity towards silica-based scale, they are particularly effective against silica-based scale.

[0006] Next, the present invention provides a method of producing the above water soluble copolymers (salts) characterized in that:

- ① monomer components comprising principally (a) a monomer containing a carboxylate group and (b)-1 a monomer containing a polyalkylene oxide group are polymerized; or
- ② during or after polymerization of a monomer component comprising principally component (a) above, a polyalkylene oxide (b)-2 is introduced by esterification; or
- ③ during or after polymerization of a monomer component comprising principally component (a) above and an active hydrogen-containing monomer, an alkylene oxide (b)-3 is reacted to introduce polyalkylene oxide groups,

so as to give weight average molecular weight exceeding 50,000 but not more than 3,000,000.

[0007] Herein, it is desirable for the ratio by weight of the above (a) / (b) [(b)-1, (b)-2 or (b)-3] to be 40~98/2~60 [such that (a)+(b) = 100 wt %]. Moreover, if the ratio by weight of the above (a) / (b) [(b)-1, (b)-2 or (b)-3] is 50~98/2~50 [such that (a)+(b) = 100 wt %], it is also desirable for the value of A expressed

by the following formula to exceed 25 but not be more than 3,000,000.

$$A = \{ (Mw/10,000)^4 \times [(wt \% \text{ of } (b) \text{ within } (a), (b))] \} / 1000$$

(wherein Mw denotes weight average molecular weight)

It is furthermore desirable for the degree of polymerization of the above polyalkylene oxide to be 2~50.

[0008]

[Embodiments of the invention] In the present invention, the scale-inhibiting effect will be inferior if condition (2) is not satisfied even though condition (1) is met. The scale-inhibiting effect will also be inferior if either of the essential components in (1) is missing even though condition (2) is met. Surprisingly, the scale-inhibiting effects are manifested synergistically as a result of limiting the functional groups and raising the molecular weight in this way and no one had previously discovered this.

[0009] The carboxylate group-containing monomers (a) for water soluble copolymers (salts) of the present invention are not particularly specified as long as they are monomers containing a carboxylate group and with a polymerizable double bond. Examples would include anhydrous maleic acid, acrylic acid, methacrylic acid,  $\alpha$ -haloacrylic acid, maleic acid, itaconic acid, vinylacetic acid, allylacetic acid, fumaric acid, phosphinocarboxylic acid,  $\beta$ -carboxylic acid or the salts thereof. Preferably they are acrylic acid, methacrylic acid or the salts thereof. These carboxylate group-containing monomers may be used singly or as mixtures of two or more types. The amount of the carboxylate group-containing monomer (a) used should preferably be 40~98% by weight, more preferably 50~98% by weight and most preferably 50~90% by weight within structural units (a)

and (b), that is to say, the monomer component comprising principally components (a) and (b). Staying within the above range is desirable from the point of view of the scale-inhibiting performance of the resulting copolymer (salt).

[0010] Furthermore, methods to introduce the structural unit with a polyalkylene oxide group (b) into a water soluble copolymer (salt) of the present invention may include the following:

- ① the above-mentioned carboxylate group-containing monomer (a) and polyalkylene oxide group-containing monomer (b)-1 are polymerized;
- ② during or after the polymerization of the above component (a), a polyalkylene oxide (b)-2 is grafted on by esterification;
- ③ during or after the polymerization of monomer component (a) above and an active hydrogen-containing monomer [including the situation in which component (a) itself contains active hydrogen], an alkylene oxide (b)-3 is reacted to introduce polyalkylene oxide groups.

[0011] If polymerizing the polyalkylene oxide group-containing monomer (b)-1 in ① above, the following may be cited as examples of this (b)-1 component;

(alkoxy) polyethyleneglycol mono(meth)acrylate,

(alkoxy) polypropyleneglycol mono(meth)acrylate,

(alkoxy) polyethyleneglycol-polypropyleneglycol  
mono(meth)acrylate,

(alkoxy) polyethyleneglycol-polytetramethyleneglycol  
mono(meth)acrylate,

(alkoxy) polypropyleneglycol-polytetramethyleneglycol  
mono(meth)acrylate.

Preferably it is (alkoxy) polyethyleneglycol  
mono(meth)acrylate, (alkoxy) polypropyleneglycol mono

(meth)acrylate or (alkoxy) polyethyleneglycol-polypropyleneglycol mono(meth)acrylate. These (b)-1 polyalkylene oxide group-containing monomers may be used singly or as mixtures of two or more types.

[0012] Moreover, when introducing polyalkylene oxide groups during or after polymerization, this may be done by esterifying (b)-2 polyalkylene oxides as in ②, or by reacting (b)-3 polyalkylene oxides during or after the polymerization of a monomer containing active hydrogen as in ③. Examples of the (b)-2 polyalkylene oxides to be introduced by esterification as in ② would be (alkoxy) polyethyleneglycol, (alkoxy) polypropylene glycol and (alkoxy) polyethyleneglycol-polypropylene glycol etc. These polyalkylene oxides used when grafting the polyalkylene oxide during or after polymerization may be used singly or as mixtures of two or more types.

[0013] When introducing polyalkylene oxide groups by reacting a (b)-3 alkylene oxide during or after the polymerization of a monomer with active hydrogen as in ③, examples of the monomer with active hydrogen would include unsaturated (meth)allylether monomers expressed by general formula (II) (at least one of Y and Z being a hydroxyl group), unsaturated alcohols, hydroxyl group-containing (meth)acrylic acid esters and (N-substituted) (meth)acrylamides etc. from amongst monomers other than components (a) and (b) copolymerizable with them. Ethylene oxide and propyleneoxide etc. may be cited as the (b)-3 alkylene oxides used. The molar ratio of ethylene/propylene in the above alkylene oxides is preferably 0~100/100~0 and more preferably 50~100 / 50~0. The above alkylene oxides may be used singly or as mixtures of two or more types.

[0014] The amount of the above component (b) [(b)-1, (b)-2 or (b)-3] used should preferably be 2~60% by weight, more preferably 2~50% by weight and most preferably 10~50% by weight within structural units (a) and (b), that is to say, components (a) and (b). Staying within this range is desirable in terms of the scale-inhibiting performance of the resulting copolymer (salt).

[0015] If the water soluble copolymers (salts) of the present invention have structural units (a) with carboxylate groups accounting for 50~98% by weight of the repeating structural units and structural units (b) with polyalkylene oxide groups accounting for 2~50% by weight of the total repeating structural units [such that (a)+(b) = 100 wt %], then it is desirable for the value of A expressed by the following formula to exceed 25 but not be more than 3,000,000.

$$A = \{(Mw/10,000)^4 \times [(wt \% \text{ of } (b) \text{ within } (a), (b))]\} / 1000$$

Thus in other words, in water soluble copolymers (salts) of the present invention, weight average molecular weight (Mw) needs to be raised further if there are few polyalkylene oxide groups. It is desirable for A to be within this range in terms of scale-inhibiting performance. Moreover, the length (degree of polymerization) of the above polyalkylene oxides is preferably 2~50 and more preferably 2~30. Staying within this range is desirable in terms of scale-inhibiting performance.

[0016] In addition to components (a)~(b), one or more other monomers capable of copolymerizing with them may also be copolymerized in the water soluble copolymers (salts) of the present invention. As examples of other such copolymerizable monomers may be cited conjugated

dienesulphonic acids expressed by general formula (I)  
(e.g. 2-methyl-1,3-butadiene-1-sulphonic acid),  
[0017]

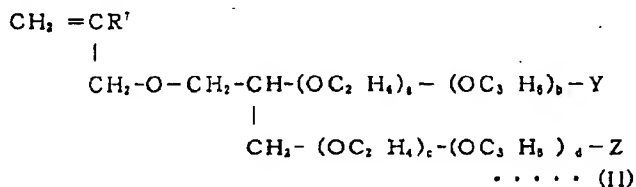
[Chem. Form. 1]



[0018] (in the formula,  $R^1 \sim R^6$  denote a hydrogen atom,  $C_{1-8}$  alkyl group,  $C_{6-20}$  aryl group or  $-SO_3X$ ; wherein X is a hydrogen atom, metal atom, ammonium group or amino group and at least one from  $R^1 \sim R^6$  is  $-SO_3X$ ),  
or unsaturated (meth)allyl ether monomers expressed by general formula (II) below (for example 3-allyloxy-2-hydroxypropanesulphonic acid, 3-methallyloxy-2-hydroxypropanesulphonic acid),

[0019]

[Chem. Form. 2]



[0020] [in the formula,  $R^7$  denotes a hydrogen atom or  $C_{1-8}$  alkyl group, a~d are the same or different and denote 0 or an integer from 1~100 (however  $a+b+c+d=0 \sim 100$ ); the  $(OC_2H_4)$  unit and  $(OC_3H_6)$  unit are bonded in any order; Y and Z are a sulphonate group or hydroxyl group and at least one from Y and Z is a sulphonate group],  
or sulphonic acids (salts) with polymerizable double bonds such as (meth)acrylamido-2-methylpropanesulphonic acid, 2-hydroxy-3-acrylamidopropane sulphonic acid, styrenesulphonic acid, methallylsulphonic acid, vinylsulphonic acid, allylsulphonic acid and isoamylenesulphonic acid; unsaturated alcohols such as vinylalcohol, allylalcohol, methylvinyl alcohol, ethylvinyl alcohol and vinylglycolic acid; hydroxyl

group-containing (meth)acrylic acid esters such as hydroxymethyl (meth)acrylate, hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, glycerol mono(meth)acrylate, glycerol di(meth)acrylate, butanediol (meth)acrylate and hexanediol (meth)acrylate; (N-substituted) (meth)acrylamides such as (meth)acrylamide and N-alkylacrylamides; aromatic compounds such as styrene,  $\alpha$ -methylstyrene, vinyltoluene and p-methylstyrene; (meth)acrylic acid alkylesters such as methyl (meth)acrylate, ethyl (meth)acrylate and octyl (meth)acrylate; aliphatic conjugated dienes such as butadiene, isoprene, 2-chlor-1,3-butadiene and 1-chlor-1,3-butadiene; and vinylcyano compounds such as (meth)acrylonitrile. If copolymerizing these other monomers, it is desirable for them not to exceed 40% by weight of total monomer components.

[0021] The following methods may be employed to produce the water soluble copolymers (salts) containing carboxylate and polyalkylene oxide groups presented in the present invention. That is, the carboxylate group-containing monomer and polyalkylene oxide group-containing monomer can be polymerized in the presence of a polymerization initiator, for example, a known radical polymerization initiator such as hydrogen peroxide, sodium persulphate or potassium persulphate at a reaction temperature normally of 20~200°C and preferably 40~150°C for 0.1~20 hours to produce the copolymer (salt). Moreover, the carboxylate group-containing monomer can be polymerized in the presence of a polymerization initiator, for example, a known radical polymerization initiator such as sodium persulphate or potassium persulphate at a reaction temperature normally of 20~200°C and preferably 40~150°C for 0.1~20 hours and after or whilst producing the copolymer, the



polyalkylene oxide is grafted on by esterification. Furthermore, the carboxylate group-containing monomer and an active hydrogen-containing monomer can be polymerized in the presence of a polymerization initiator, for example, a known radical polymerization initiator such as sodium persulphate or potassium persulphate at a reaction temperature normally of 20-200°C and preferably 40-150°C for 0.1-20 hours and after or whilst producing the copolymer, an alkylene oxide is reacted to introduce polyalkylene oxide groups. The molecular weight of the copolymer (salt) obtained can be regulated by controlling the reaction conditions and especially the amount of polymerization and reaction solvents, type and quantity of polymerization initiator, reaction temperature and the like at this time.

[0022] Polymerization and reaction solvents can be used to make the above reactions proceed smoothly. Water, organic solvents or mixtures of water and organic solvents miscible with water may be used as these polymerization and reaction solvents. Specific examples of such organic solvents would include alcohols such as methanol, ethanol, propyl alcohol and butanol, aromatic hydrocarbons such as benzene, toluene, xylene and ethylbenzene, aliphatic hydrocarbons such as n-pentane, n-hexane, cyclohexane, n-heptane or octane or ethers such as diethylether, tetrahydrofuran and 1,4-dioxane. The above polymerization and reaction solvents are used in amounts 0-100 times the solid weight of the water soluble copolymer (salt) of the present invention. When polymerizing the monomer components in the above reactions, the whole of the monomer components may be added as one charge to the reaction vessel or some or all of the monomer components may be added gradually. The amount of polymerization initiator relative to total

monomers is normally 0.001-20% by weight and preferably 0.01-10% by weight.

[0023] The water soluble copolymers (salts) containing carboxylate groups and polyalkylene oxide groups provided by the present invention need to have weight average molecular weight exceeding 50,000 but not more than 3,000,000. If the weight average molecular weight is less than 50,000, the scale-inhibiting effect deteriorates but there are problems if it exceeds 3,000,000 such as that the material becomes difficult to manufacture.

[0024] There are no particular restrictions on the type of cations in the water soluble copolymers (salts) thus obtained, but in order to ensure water solubility, it is desirable for them to be hydrogen, alkali metals, alkali earth metals, ammonium or amines. Illustrations of the above alkali metals would include sodium, potassium etc.; of the alkali earth metals, calcium, magnesium etc.; of the amines, alkylamines such as methylamine, ethylamine, propylamine, dimethylamine, diethylamine, triethylamine, butylamine, dibutylamine and tributylamine, polyamines such as ethylene diamine, diethylene triamine and triethylene tetramine; morpholine and piperazine etc. Preferably they are hydrogen, sodium or potassium. These cations may be mutually exchanged with other types of cation by a variety of ion exchange techniques.

[0025] The structure of the water soluble copolymers (salts) of the present invention can be confirmed by infrared spectroscopy from carboxylate group absorption at  $1700\sim1800\text{ cm}^{-1}$  and polyalkylene oxide group absorption at  $1050\sim1150\text{ cm}^{-1}$  or by NMR. The compositional ratio can also be confirmed by determining the levels of carboxylate and undertaking elemental analysis.

[0026] If using a water soluble copolymer (salt) of the present invention as a scale inhibitor, as long as the active ingredient is a water soluble copolymer (salt) with carboxylate and polyalkylene oxide groups as essential components and weight average molecular weight exceeding 50,000 but not more than 3,000,000, it may incorporate components other than these. The water soluble copolymer (salt) of the present invention is added just as it is, or dissolved in water etc., to boiler water systems, geothermal water systems, open or closed circuit cooling water systems and single pass cooling water systems and the like. The amount added will vary depending on the concentration of metal ions and silica in the target water system, but generally will be about 1~200 mg per litre. By adding a water soluble copolymer (salt) of the present invention as a scale inhibitor to the target water system, scale is controlled not only by inhibiting the formation of metal salt scales such as calcium or magnesium salts and silica-based scale, but also by removing existing scale. They are particularly effective against silica-based scale. When being used as scale inhibitors, the water soluble copolymer (salt) of the present invention may be used concomitantly with other scale inhibitors, anticorrosion agents and slime inhibitors.

[0027]

[Examples] The invention is described in more specific terms through the examples but is not limited to the following examples. The terms 'parts' and '%' in the examples are based on weight unless specified otherwise. Weight average molecular weight (Mw) in the examples was calculated by converting the results determined by gel permeation chromatography (GPC) using a calibration curve prepared taking sodium polystyrenesulphonate as

the standard sample. The GPC conditions were as follows.

Column: ① G3000PWXL (Tosoh)

Column: ② GMPWXL (Tosoh)

Column: ③ GMPWXL (Tosoh)

Columns ①~③ were connected in order in linear fashion and the sample was introduced from the column ① side.

Detector: Differential refractometer RI-8021 (Tosoh)

Eluent: water/acetonitrile/sodium sulphate = 2, 100/900/15 (ratio by weight)

Flow rate: 1.0 mL/min

Temperature: 40°C

Sample concentration: 0.2%

Sample injection volume: 400µL

[0028] Reference Example 1

Having added 99.4 g of an 80% aqueous solution of acrylic acid, 70.6 g of methoxypolyethyleneglycol monomethacrylate and 15.0 g of 35% aqueous hydrogen peroxide to a one litre capacity vessel containing 417.5 g of water over a period of one hour whilst stirring under reflux conditions, the material was aged for two hours under reflux conditions and a copolymer (salt) was obtained.

[0029] Reference Example 2

Having added 120.4 g of an 80% aqueous solution of acrylic acid, 49.6 g of methoxypolyethyleneglycol monomethacrylate and 14.6 g of 35% aqueous hydrogen peroxide to a one litre capacity vessel containing 401.6 g of water over a period of one hour whilst stirring under reflux conditions, the material was aged for two hours under reflux conditions and a copolymer (salt) was obtained.

[0030] Reference Example 3

Having added 151.8 g of an 80% aqueous solution of acrylic acid, 18.2 g of methoxypolyethyleneglycol monomethacrylate and 16.3 g of 35% aqueous hydrogen peroxide to a one litre capacity vessel containing

351.7 g of water over a period of one hour whilst stirring under reflux conditions, the material was aged for two hours under reflux conditions and a copolymer (salt) was obtained.

[0031] Reference Example 4

Having added 151.8 g of an 80% aqueous solution of acrylic acid, 18.2 g of methoxypolyethyleneglycol monomethacrylate and 23.3 g of 35% aqueous hydrogen peroxide to a one litre capacity vessel containing 499.9 g of water over a period of one hour whilst stirring under reflux conditions, the material was aged for two hours under reflux conditions and a copolymer (salt) was obtained.

[0032] Polymer A

Having added 40.9 g of an 80% aqueous solution of acrylic acid, 29.1 g of methoxypolyethyleneglycol monomethacrylate and 10.3 g of 35% aqueous hydrogen peroxide to a one litre capacity vessel containing 522.8 g of water over a period of ten hours whilst stirring under reflux conditions, the material was aged for two hours under reflux conditions and a copolymer (salt) was obtained.

Polymer B

Polyacrylic acid

[0033]

The composition and weight average molecular weight (Mw) of the polymers used in the examples and comparative examples are set out in Table 1.

[0034]

Table 1

	Weight ratio of structural units with carboxylate / polyalkylene oxide groups	Weight average molecular weight (Mw)	A value
Ref. Ex. 1	47 / 53	409,000	131,520
Ref. Ex. 2	34 / 66	480,000	180,486
Ref. Ex. 3	13 / 87	802,000	10,813
Ref. Ex. 4	13 / 87	62,000	19
Polymer A	47 / 53	32,000	5
Polymer B	0 / 100	256,000	0

[0035] Examples 1~4, Comparative Examples 1~3

Yokohama municipal water was added as the circulating and top-up water to an open circuit type of cooling water system with holding capacity of 0.45 m<sup>3</sup> and a heat exchanger with an electrically heated area of approximately 0.25 m<sup>2</sup>. This was operated for 30 days controlling the concentration factor to 5-fold. The heat exchanger was made of SUS304 with a circulating water inlet temperature of 30°C, outlet temperature of 50°C and flow rate of 0.5 m/s. The circulating water was of pH 9.0 with electrical conductivity of 1050 µS/cm and had calcium hardness of 250 mg/L (as CaCO<sub>3</sub>), magnesium hardness of 125mg/L (as CaCO<sub>3</sub>), silica concentration of 150 mg/L (as SiO<sub>2</sub>) and M alkalinity of 250 mg/L (as CaCO<sub>3</sub>). The specific amounts of the scale inhibitors in Table 1 were added to this water system and the rate of scale deposition onto the heat exchanger tubes was measured. The results are shown in Table 2. It is evident from the results in Table 2 that the scale-inhibiting effects achieved with the materials in the Examples were greatly superior to those in the Comparative Examples.

[0036]

Table 2

	Agent used	Agent concentration (mg/mL)	Rate of scale deposition (mg/cm <sup>2</sup> /month)
Examples	Ref. Ex. 1	15	1.9
	Ref. Ex. 2	15	1.5
	Ref. Ex. 3	15	1.7
	Ref. Ex. 4	15	4.6
Comparative Examples	Polymer A	15	23.8
	Polymer B	15	20.5
	None		22.6

[0037]

[Advantages of the invention] If a water soluble copolymer (salt) of the present invention with carboxylate groups and polyalkylene oxide groups as essential components and moreover weight average molecular weight exceeding 50,000 but not more than 3,000,000 is used as a scale inhibitor, it provides highly effective inhibition of scale, and especially silica-based scale, and the scale-inhibiting effects can be maintained for long periods of time.

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(51) Int.Cl <sup>7</sup>	Identification Code	FI	Theme Code (Ref).
C 08 F 22/00		C 08 F 22/00	
290/06		290/06	
C 23 F 14/02		C 23 F 14/02	A

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F terms 4J027 AC02 AC03 AC04 AC06 AC09  
(ref) AJ01 AJ08 BA02 BA03 BA04  
BA05 BA06 BA07 BA08 BA13  
BA14 BA17 BA19 CB02 CC02  
4J100 AJ01P AJ02P AJ03P AJ08P  
AJ09P AK32P AL08Q BA04Q  
BA08Q BA09Q CA04 DA00  
DA01 JA21  
4K062 AA03 BC13 BC14 BC19 CA04  
FA04 FA05 FA06 GA10

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